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ANG 567 :50

September 28, 1961

Office of Ordnance Research U. S. Army Box CM, Duke Station Durham, North Carolina

62-1-2

XEROX

Ordnance Project: Number TB-2-0001-567

Title of Project: Nucleophilic Attack of Aromatic Rings by Organometallic Compounds

Gentlemen:

This is the Final Report on Contract No. DA-11-022-ORD-874. Among the discoveries made the following may be mentioned. Addition of organometallic compounds to hindered ketones involving aromatic rings has been achieved in both the 1,4- and 1,6-manner with and without displacement of groups. Addition is greatly facilitated by the presence of a hydroxyl group in an o- or pposition of the aromatic ring. Similar results have been observed with anils of benzophenones. New routes to terphenyls and to isobenzofurans have been discovered. The first example of addition of an organolithium compound in the 1,6-manner has been recorded. In this connection side chain metabation has been noted. Keto organolithium and organomagnesium compounds have been studied. Transcarbonylation has been used in a synthetic route to ketones.

The following published papers were based on work done under this contract.

- Condensation of t-Butylmagnesium Chloride with α,β,β-Triphenylachylophenone. Reynold C. Fuson and Lewis I Krimen, J. Am. Chem. Soc., 77, 994 (1955).
- The Condensation of t-Butylmagnesium Chloride with Duryl o-2. Isopropenylphenyl Ketone. Reynold C. Fuson, William D. Emmons and Shaler G. Smith, Jr., J. Am. Chem. Soc., 77, 2503 (1955).
- Conjugate Bimolecular Reduction of Hindered Ketones Involving 3. Replacement of Methoxyl Groups. III.
 Reynold C. Fuson, George W. Parshall and Earl H. Hess, J. Am. Chem. Soc., 77, 3776 (1955).
- 4. Conjugate Addition of t-Butylmagnesium Chloride to o-Hydroxy Diaryl Ketones. Reynold C. Fuson and Fabian T. Fang, J. Am. Chem. Soc., 77, 3781 (1955).

- 5. The Reaction of Grignard Reagents with the Anils of Benzophenone and o-Methoxybenzophenone.

 Reynold C. Fuson, Robert J. Lokken and Rudolph L.

 Pedrotti, J. Am. Chem. Soc., 78, 6064 (1956).
- 6. Selective Side Chain Metalation of Duryl o-Tolyl Ketone.
 Reynold C. Fuson, William C. Hammann and Paul R. Jones,
 J. Am. Chem. Soc., 79, 928 (1957).
- 7. The Action of Phenylmagnesium Bromide on 10,10-Diphenyl-9,10-dihydro-9-phenanthrone.

 Reynold C. Fuson and Paul T. Tomboulian, J. Am. Chem. Soc., 79, 956 (1957).
- 8. 1,4-Addition of Grignard Reagents to 9-Phenanthryl Ketones.
 Reynold C. Fuson and Stanley J. Strycker, J. Am. Chem.
 Soc., 79, 2633 (1957).
- 9. Isomerization of 1,4-Dibenzoyl-1,4-dimesitolybutane.
 Reynold C. Fuson and H. Scott Killam, J. Org. Chem.,
 22,845 (1957).
- 10. Duryl 2,6-Disubstituted Phenyl Ketones.

 Reynold C. Fuson and Bruno Vittimberga, J. Am. Chem.
 Soc., 79, 6030 (1957).
- 11. Keto Grignard Reagents. Intramolecular Reduction.
 Reynold C. Fuson and Norman Shachat, J. Org. Chem., 22, 1394 (1957).
- 12. The Action of Grignard Reagents on β-Substituted Propiomesitylenes.
 Reynold C. Fuson, Earl H. Hess and H. Scott Killam, J. Org. Chem., 23, 645 (1958).
- 13. Organometallic Compounds from Aryl Halides Containing Ether Functions.

 Reynold C. Fuson and Bernard Freedman, J. Org. Chem., 23, 1161 (1958).
- 14. Synthesis of 2-Iodo-2'-methoxybiphenyl. A New Route to o-Terphenyls.

 Reynold C. Fuson and Pobert L. Albright, J. Am. Chem. Soc., 81, 487 (1959).
- 15. Pyrolysis of the 1,4-Addition Products Obtained from 1-Naphthyl Trityl Ketone and Grignard Reagents.

 Reynold C. Fuson and K. Darrell Berlin, J. Am. Chem. Soc., 81, 2130 (1959).
- 16. 1,6-Addition of n-Butyllithium to Hindered Diaryl Ketones.

 Reynold C. Fuson and John R. Larson, J. Am. Chem. Soc.,
 81, 2149 (1959).

- 17. A Synthesis of Symmetrical Diaryl Ketones by a Transcarbonylaction Reaction.

 Reynold C. Fuson, Gerald R. Bakker and Bruno Vittimberga, J. Am. Chem. Soc., 81, 4858 (1959).
- 18. Ring Interconversion by Transacylation in the Benzofluorenone and Benzanthrone Series.

 Reynold C. Fuson, William A. Hills and Bruno Vittimberga, J. Am. Chem. Soc., 82, 2559 (1960).
- 19. Autoxidation of the Enol Form of 1,2-Dimesitoylcyclohexane.

 A New Route to Epoxy Ketones.

 Reynold C. Fuson, William R. Hatchard, Roger H. Hottke, and James L. Fedrick, J. Am. Chem. Soc., 82, 4330 (1960).
- 20. Conjugate Bimolecular Reduction of Hindered Ketones Involving Replacement of Methoxyl Groups. IV. Mesityl 2-Methoxy-1-naphthyl Ketone.

 Reynold C. Fuson and David E. Frankhouser, J. Org. Chem., 25, 1498 (1960).
- 21. Action of Acid on o-Aroyldiarylcarbinols. A New Route to Isobenzofurans.

 Reynold C. Fuson and William C. Rife, J. Org. Chem., 25, 2226 (1960).
- 22. Demethoxylation of Hindered o-Methoxy Ketones.

 Reynold C. Fuson, Bruno Vittimberga and David E.

 Frankhouser, J. Org. Chem., 26, 582 (1961).
- 23. 1,6-Reductive Coupling of Hindered o-Vinyl Diaryl Ketones.
 Reynold C. Fuson, Earl H. Hess and Mehm Tin Mon, J.
 Org. Chem., 26, 1042 (1961).
- 24. Intramclecular Condensation of 2-Biphenylylglyoxal.

 Reynold C. Fuson and Richard L. Talbott, J. Org. Chem.,
 25, 2674 (1960).

The following papers are in press or in preparation; Technical Reports on these will be made when the reprints become available.

- 1. Addition of Benzylmagnesium Chloride and p-Chlorobenzylmagnesium Chloride to Phenyl Duryl Ketone. Reynold C. Ruson, Jeremiah P. Freeman and Jerome J. Looker, J. Org. Chem. (in press).
- 2. Evidence for 9-Methylene-10-acetoxy-10-methyl-9,10-dihydro-phenanthrene as an Intermediate.
 William E. Adcock, J. Org. Chem. (in press).

- 3. Addition of Aryl Grignard Reagents to 3-Benzoylfurans.

 Reynold C. Fuson, H. Scott Killam and William S. Smith,

 Jr. (in preparation).
- 4. Condensation of Chalcone with Phenylmagnesium bromide. 2-Benzohydryl-3-hydroxy-3,3-diphenylpropionic Acid.
 Reynold C. Fuson, M. Thet San and Jürgen Diekmann (in preparation).

These and any other papers will be made the subject of Technical Reports when reprints become available.

Respectfully submitted,

R. C. Fuson

Principal Investigator

R.C. Fuson

RCF: jkj